

## Metal-insulator transition in the compensated sodium bronze, $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$

M. A. Dubson\* and D. F. Holcomb

*Materials Science Center and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*

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We have measured the dc electrical conductivity  $\sigma$  of cubic  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  from 1.6 to 295 K for various values of  $x$  and  $y$ . A sample with  $x-y=0.18$  appears to fall directly at the metal-insulator transition and shows an unusual temperature dependence,  $\sigma(T) \propto T$ , from 1.6 K to room temperature. A model for  $\sigma(T)$  based on the scaling theory of localization, when used to interpret the data on this and other samples, gives a conductivity exponent  $\nu$  of 1.0. This model assumes that  $\sigma(T)$  is controlled by a thermal smearing of the occupancy of one-electron energy states near the Fermi level rather than by inelastic scattering. Comparison of the conductivity transition in  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  with earlier data for the uncompensated material  $\text{Na}_x\text{WO}_3$  indicates that the additional disorder introduced by Ta doping does not shift the critical value of electron concentration.

### I. INTRODUCTION

The nonstoichiometric compound  $\text{Na}_x\text{WO}_3$  (commonly called sodium tungsten bronze) undergoes<sup>1</sup> a transition from semiconducting to metallic behavior as  $x$  is increased through an  $x$  value of about 0.20. A thorough experimental characterization of the transition has been inhibited by the fact that there are several changes in the equilibrium crystal structure in the  $x$  range of interest. In 1978 Doumerc *et al.*<sup>2</sup> discovered that the tantalum-doped bronze  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  also undergoes a metal-insulator ( $M-I$ ) transition but that the cubic crystal phase can be produced on both sides of the transition. The transition occurs when the composition parameter  $x-y$  is about 0.2. Doumerc proposed that the conduction-electron concentration in the metal is proportional to  $x-y$ , that is, that the Na atoms act as donors and Ta atoms act as acceptors. The Ta-doped bronze can thus be regarded as a heavily-doped, compensated semiconductor.

Band-structure calculations and Hall measurements<sup>3</sup> indicate that all Na atoms act as electron donors in metallic  $\text{Na}_x\text{WO}_3$ . Doumerc's argument that Ta atoms act as acceptors in the Ta-doped bronze is simple. Tantalum is one place to the left of tungsten in the Periodic Table; it has one less electron. So when tantalum substitutes for tungsten it must take an electron from the conduction band in order to complete the covalent bonds with its oxygen neighbors. Although there is compelling semiquantitative evidence for Doumerc's  $x-y$  model,<sup>4</sup> there exists no direct experimental confirmation such as Hall coefficient measurements.

We have prepared a set of samples of the tantalum-doped material and we have made measurements of dc conductivity  $\sigma$  as a function of composition and temperature. Our conductivity data complement the previous measurements of Doumerc *et al.*<sup>2,5</sup> We have also made an extensive set of NMR measurements on the  $^{183}\text{W}$  spin system. The purpose of this paper is to report our conclusions about the characteristics of localization in doped and compensated materials such as this bronze. Our conclusions are drawn primarily from the conductivity mea-

surements.

(1) We have found that the conductivity of a sample with  $x-y=0.18$  shows an unusual temperature dependence,  $\sigma(T) \propto T$ , from 1.6 K to 295 K. This sample divides those at larger values of  $x-y$  which are metallic from those at lower values of  $x-y$  which exhibit insulating properties. [We define a metal as a material in which  $\sigma(T \rightarrow 0) > 0$ .] We will show that a model based on a simple application of the Kubo formalism and the scaling theory of localization<sup>6,7</sup> can reproduce the linear  $T$  dependence and provides a natural explanation of the temperature dependence of  $\sigma$  for several samples with compositions near the critical composition for the  $M-I$  transition. The temperature dependence of  $\sigma$ , when interpreted in the light of our model, permits a very sensitive determination of the critical sample composition,  $(x-y)_c$ .

(2) Comparison of our values of  $\sigma(x-y)$  with values of  $\sigma(x)$  previously measured for  $\text{Na}_x\text{WO}_3$  by various workers<sup>3</sup> suggests that the  $M-I$  transition in this material is governed by the density of uncompensated Na atoms rather than by a certain threshold of "disorder." Near the transition, very strong electron scattering in the Ta-compensated material lowers the conductivity by nearly a factor of ten in comparison to values of  $\sigma$  in the uncompensated  $\text{Na}_x\text{WO}_3$  at the same electron concentration,  $x-y$ . Yet the  $M-I$  transition appears to occur at the same value of  $x-y$  in both materials. This insensitivity of the value of critical composition to the introduction of a substantial degree of disorder via the tantalum substitution argues against a broad-brush description of the transition as an "Anderson transition."

### II. EXPERIMENTAL PROCEDURES

The samples are prepared in two stages. First, large metallic single crystals about a centimeter on a side with composition  $x=0.60$ ,  $y=0.16$  are grown by fused salt electrolysis. After fragmenting of the large crystals, some of the sodium is diffused out in a process that involves baking at high temperatures. The final products are single-crystal chips with dimensions less than  $2 \times 1 \times 0.3$

mm. By a combination of electron-probe microanalysis and precise lattice parameter measurements, the values of  $x$  and  $y$  are determined with an absolute accuracy of  $\pm 0.01$ . The crystals have high homogeneity, with  $x$  and  $y$  varying by less than 0.005 over the sample volume. Procedures for the manufacture of  $\text{Na}_x\text{WO}_3$  are relatively straightforward and can be found in the literature.<sup>8,9</sup> However, we have found that the production of high-quality samples of the Ta-doped bronze is much more difficult. The chemical homogeneity and mechanical quality of the Ta-doped bronze are painfully sensitive<sup>4</sup> to several experimental parameters including the crystal growth temperature, the electrolytic current, the duration of the electrolytic growth, the electrode configuration, the electrode materials, the crucible material, the diffusion bake temperature and duration, etc.

The dc electrical conductivity of single-crystal chips was measured with a simple four-point probe circuit. Current was provided by a Keithley model 225 constant current source and the signal from the voltage leads was measured with a Keithley model 181 nanovoltmeter. The crystal was held in place on a sample holder by two gold-plated brass blocks serving as current leads, one of them spring-loaded. The voltage leads make electrical connection with the sample through two gold-plated, spring-loaded needle probes. The contact resistance of a lead pressed against a metallic sample was typically one or two  $\Omega$ , while the resistance of the metallic sample itself is around 0.01  $\Omega$ . With insulating samples, the contact resistance is a hundred  $\Omega$  or more, while the sample resistance is typically  $k\Omega$ .

Resistance measurements were made at room temperature, 77 K, 4.2 K, and in the sub-4.2 K region down to 1.6 K. Low-temperature measurements were made with the sample immersed directly in the cryogenic fluid.

To avoid self-heating, the sample current was kept sufficiently low that the Joule heating power due to the resistance of the sample and contacts was less than  $10^{-6}$  watts. Self-heating was unlikely, since the sample was immersed directly in the cryogenic fluid, but, as a check, the sample resistance was measured with two or more different currents to ensure that the result was independent of current.

Upon thermal cycling between room temperature and 1.6 K, the resistance of each sample was reproducible to within 2%. This 2% drift may be caused by a slight slipping of the voltage contacts on the sample as a result of thermal stress. Because the single-crystal chips are somewhat irregularly shaped, the absolute value of the conductivity could only be determined to within about 15%.

### III. CONDUCTIVITY IN THE Ta-DOPED BRONZE

Figure 1 shows conductivity as a function of temperature for a series of samples that span the  $M-I$  transition. Also shown in Fig. 1 is the value of Mott's minimum metallic conductivity,<sup>10</sup>  $\sigma_{\min} = Be^2 n_c^{1/3} / \hbar$ , where the constant  $B$  is taken to have the value 0.05, and  $n_c$  is the critical uncompensated donor density.

A few comments about the information given in Fig. 1 are in order. On the basis of the analysis to be discussed

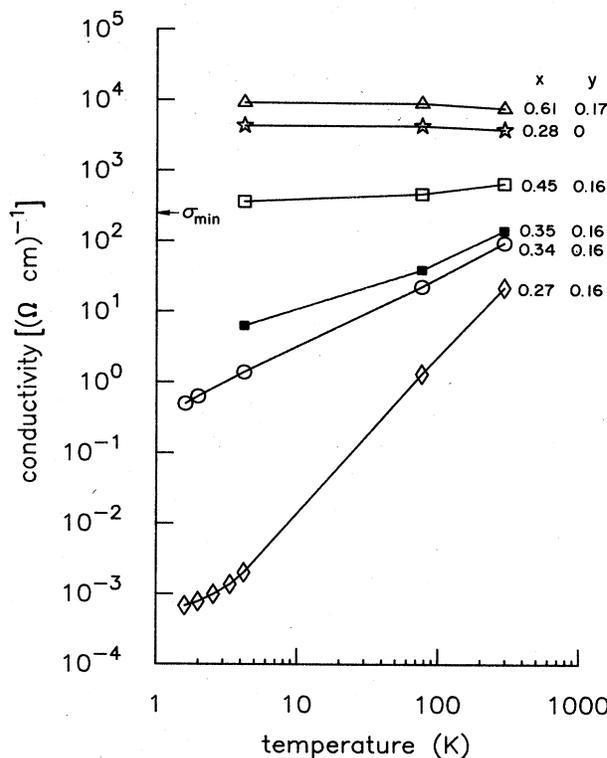


FIG. 1. Conductivity versus temperature for several samples of  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$ .

subsequently, we place the  $M-I$  transition at  $x - y = 0.18$ . Thus, our sample with  $x = 0.27, y = 0.16$  ( $x - y = 0.11$ ) and that of Doumerc *et al.* with  $x = 0.29, y = 0.23$ , ( $x - y = 0.06$ ) should have  $\sigma \rightarrow 0$  as  $T \rightarrow 0$ . However, a smooth extrapolation of the existing data to lower temperature appears likely to give  $\sigma > 0$  at  $T = 0$  for both samples. Nevertheless, we regard these samples as insulators since their low-temperature conductivity is approximately  $5 \times 10^{-4} (\Omega \text{ cm})^{-1}$ , a value some 6 orders of magnitude below  $\sigma_{\min}$ . Evidently, some weak temperature-independent conduction mechanism dominates the thermally-activated conduction mechanisms at low temperature. Although one can speculate about conduction by surface states or by very low-mobility polarons, we have no satisfactory explanation for this anomalous behavior which has been observed by both experimental groups.

Figure 2 is a log-log plot of  $\sigma$  versus  $T$  for four samples with compositions near the critical composition for the  $M-I$  transition. Data for samples 2 and 3 of Fig. 2 also appear in Fig. 1. Samples 1 and 2 are from an early batch with poor homogeneity in which  $x$  varied by 0.01 to 0.02. Samples 3 and 4 are from a later batch and have better homogeneity, with variations in  $x$  less than 0.005. In all of the samples, variations in  $y$  are less than 0.005. Our sample analysis techniques could not clearly resolve any composition differences between samples 1 and 2 (both are  $x \cong 0.35, y \cong 0.16$ ) or between sample 3 and 4 (both are  $x \cong 0.34, y \cong 0.16$ ). Note, however, that the low-temperature conductivity of nominally identical samples

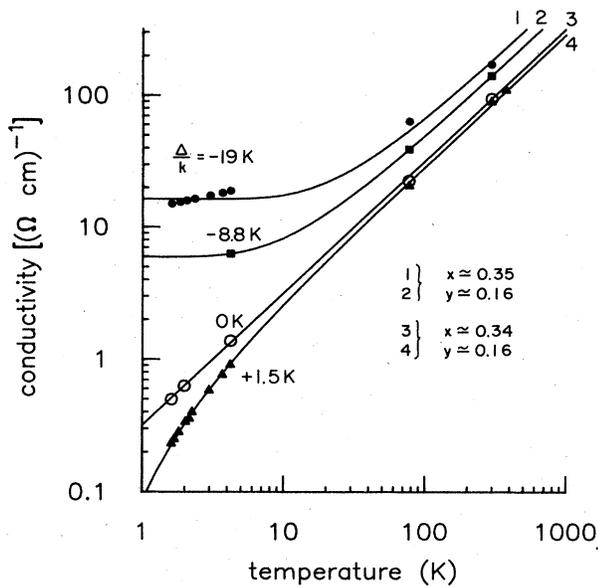


FIG. 2. Conductivity versus temperature for four samples of  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$ . The lines through the data are fits to the relationship  $\sigma(T) \propto T \ln(1 + e^{-\Delta/kT})$ . Sample 2 cracked during the handling before data below 4.2 K could be obtained.

indicates the existence of small, uncontrolled composition differences among samples from the same batch.

#### IV. A MODEL FOR $\sigma(T)$

We build upon the scaling theory of localization<sup>6</sup> put forth by Abrahams, Anderson, Licciardello, and Ramakrishnan. In that theory, the macroscopic dc conductivity of a barely metallic sample at  $T=0$  K may be written<sup>11</sup> as

$$\sigma(T=0) = (0.1) \frac{e^2}{\hbar \xi}, \quad (1)$$

where  $\xi$ , the coherence length, diverges at the  $M-I$  transition. At finite temperatures, several effects come into play to modify the scaling theory result. Imry<sup>7</sup> discusses two of these effects. (1) Thermal excitation of electrons to energy levels above the Fermi energy may alter the value of  $\xi$ , and (2) inelastic scattering may disrupt the  $T=0$  K scaling picture. If the inelastic scattering length,  $l_{in}$ , becomes smaller than  $\xi$ , then the scaling-theory picture is short-circuited and the conductivity increases over the scaling-theory value.

Our model invokes the thermal excitation mechanism noted above, but does not include the effects of inelastic scattering. We shall later give some argument that such neglect may well be valid for our material, but we note that this neglect does limit the realm of applicability of our model.

To describe the temperature dependence of the conductivity of samples near the transition, we work within the one-electron approximation and use the Kubo-Greenwood formula<sup>12</sup>

$$\sigma(T) = - \int_0^\infty \sigma_E \frac{\partial f}{\partial E} dE, \quad (2)$$

where  $\sigma_E$  is the contribution to the conductivity from

electrons at energy  $E$ , and  $f$  is the Fermi distribution function,

$$f(E) = \frac{1}{\exp[(E - E_F)/kT] + 1}. \quad (3)$$

$E_F$  is the Fermi energy. We ignore the small difference between the Fermi energy and the chemical potential for  $T > 0$ . According to the scaling theory of localization,<sup>6,13,14</sup> the zero-temperature dc electrical conductivity of a barely metallic three-dimensional system obeys the relation

$$\sigma(T=0) \propto (E_F - E_c)^\nu \propto (n - n_c)^\nu, \quad (4)$$

where  $E_c$  is the energy of a mobility edge separating localized and extended states in the one-electron density of states,  $n$  is the composition parameter of interest (concentration of uncompensated donors in this case), and  $n_c$  is the critical composition. According to the original work of Abrahams *et al.*<sup>6</sup> and the later work of McMillan,<sup>13</sup> the critical exponent  $\nu$  is approximately 1. Equation (4) is expected to be valid throughout a critical regime bounded by the  $M-I$  transition on one side (where  $E_F = E_c$ ), and on the other side by the composition at which  $\sigma \cong \sigma_{\min}$ .

In the context of the scaling theory,  $\sigma_{\min}$  is defined as the value of  $\sigma(T=0)$  obtained from Eq. (1) by setting  $\xi$  equal to the microscopic length scale,  $1/n_c^{1/3}$ . Apart from the somewhat arbitrary numerical coefficient, this definition is identical to our earlier definition of  $\sigma_{\min}$ .

On the basis of Eq. (4), we assume the  $\sigma_E$  in Eq. (2) is proportional to  $(E - E_c)^\nu$  in the range  $E_c < E < E_0$ , where  $E_0$  is the value of  $E_F$  at which  $\sigma(T=0) = \sigma_{\min}$ . We can then write

$$\sigma(T) \propto - \int_{E_c}^\infty (E - E_c)^\nu \frac{\partial f}{\partial E} dE. \quad (5)$$

Note that the term  $\partial f / \partial E$  cuts off the integral within a few  $kT$  of  $E_F$ . Thus, for  $E_c$  close to  $E_F$ , and at low enough temperatures, only the energy range  $E_c < E < E_0$  contributes to the integral. In setting the lower limit of integration at  $E_c$ , we are assuming that the conductivity due to hopping is negligible compared to that due to carriers in extended states.

Suppose now that we have a sample for which  $E_F = E_c$ , that is, one with the critical composition for the  $M-I$  transition. In this case, Eq. (5) yields  $\sigma(T) \propto T^\nu$ . Consider sample 3 of Fig. 2. A fit of the data for sample 3 to an equation of the form  $\sigma(T) = AT^\alpha$  yields  $\alpha = 0.99 \pm 0.01$ . Our model allows one to conclude that sample 3 sits extremely close to the transition and that the critical exponent  $\nu$  is 1.0.

With  $\nu = 1$ , evaluation of the integral in Eq. (5) yields

$$\sigma(T) \propto T \ln(1 + e^{-\Delta/kT}), \quad (6)$$

where  $\Delta = E_c - E_F$ . As the temperature increases, we expect this behavior to continue until  $kT = E_0 - E_F$ , at which point values of  $\sigma_E$  near  $\sigma_{\min}$  contribute significantly to the integral and  $\sigma(T)$  approaches  $\sigma_{\min}$ . The lines through the data in Fig. 2 are fits to Eq. (6), with  $\Delta$  as a free parameter.

In addition to its ability to reproduce the temperature

dependence of sample 3, the most interesting result of our model is its ability to give naturally the form of  $\sigma(T)$  for sample 4, a sample with the same nominal composition as sample 3, but apparently lying just on the insulating side of the transition. Data taken on a third sample from the same, high-quality batch that produced samples 3 and 4 gave results nearly identical to those for sample 3. The conductivity of this third sample closely followed  $\sigma(T) \propto T^\alpha$  with  $\alpha = 0.96 \pm 0.02$ .

The fit to the sparse data for sample 2 shows that the data for that sample are consistent with the model, but the fit is otherwise not very revealing. Unfortunately, this sample cracked during handling before data below 4.2 K could be obtained. Data for sample 1, farther from the transition and known to be less homogeneous in composition than 3 and 4, are not well fit by our model.

It is worth repeating that Eq. (5) is valid only within a rather narrow composition range centered about the critical composition. Deep on the insulating side of the transition (for instance, the  $x = 0.27$ ,  $y = 0.16$  sample in Fig. 1), we expect hopping conduction to dominate the conduction due to carriers thermally activated to extended states. On the metal side of the transition the assumptions behind Eq. (5) break down for  $\sigma > \sigma_{\min}$ .

We wish to emphasize the following points. This model predicts that  $\sigma(T) \propto T^\nu$  for a sample with the critical composition, so that one can extract the conductivity exponent  $\nu$  from measurements on a single well-chosen sample. For our system,  $\nu = 1$ , which is in agreement with the predictions of Abrahams *et al.* and McMillan. Finally, the exquisite sensitivity of  $\sigma(T)$  to  $\Delta$  at low temperatures allows one to precisely locate the critical composition without the need for extremely low-temperature (mK) measurements.

On rather general grounds, one might expect other temperature dependent contributions to  $\sigma(T)$  not considered in our model to appear in the higher temperature regime of Fig. 2. We cannot, of course, rule out the possibility that the apparently continuous slope of unity for sample 3 results from a combination of the effects of  $\xi(T)$  at low temperature and some other contribution at higher temperatures. However, in considering such a possibility, one needs to remember, that  $\sigma < \sigma_{\min}$  for all the data of Fig. 2. Thus any other scattering mechanisms which might affect  $\sigma(T)$  must be treated in the diffusion, or strong-scattering, regime.

The analysis of Fig. 2 identifies the composition of sample 3 as critical, thus,  $(x - y)_c = 0.18 \pm 0.01$ . If one wished to confirm our value of  $(x - y)_c$  by a more direct experimental determination, one would need data at lower temperatures. The study of Si:P by Rosenbaum *et al.*<sup>14</sup> showed the need for mK measurements in order to experimentally determine the zero-temperature conductivity unambiguously.

We now turn to the issue of the effect of inelastic scattering on  $\sigma(T)$ . Imry<sup>7,15</sup> has argued that  $\xi$  in Eq. (1) should be replaced by  $l_{\text{in}}$ , the inelastic scattering length, when the temperature is so high that  $l_{\text{in}} \ll \xi$ . Thus,

$$\sigma(T > 0) \simeq (0.1) \frac{e^2}{\hbar l_{\text{in}}}, \quad l_{\text{in}} \ll \xi. \quad (7)$$

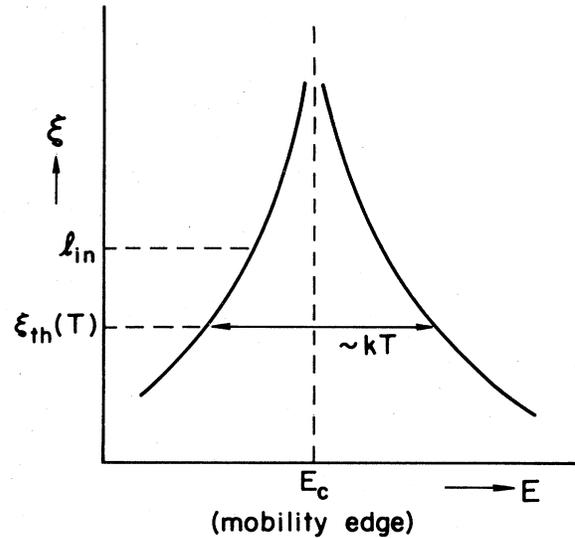


FIG. 3. The solid lines display the coherence length  $\xi$  as a function of electron energy  $E$  at  $T = 0$  K. At the  $M-I$  transition,  $E_F = E_c$ . For  $T > 0$ , the thermal coherence length,  $\xi_{\text{th}}(T)$ , is the value of  $\xi$  at the distance  $\sim kT$  from  $E_F$ . The case  $l_{\text{in}} > \xi_{\text{th}}(T)$  is shown.

Near the  $M-I$  transition,  $\xi$  is very large so that the condition  $l_{\text{in}} \ll \xi$  is satisfied at all but the very lowest temperatures.

We suggest, however, that for  $T > 0$  the relevant length scale is not the  $T = 0$  K coherence length,  $\xi$ , but rather a thermally-averaged coherence length  $\xi_{\text{th}}$ , which is determined by a suitable average over those one-electron states within  $kT$  of  $E_F$  (see Fig. 3). Note that both  $\xi_{\text{th}}$  and  $l_{\text{in}}$  are functions of temperature.

We expect that the model we have developed will be valid when  $l_{\text{in}} \gg \xi_{\text{th}}(T)$ . Our approach in examining the validity of that inequality will be to assume our model to be correct, thus permitting us to determine values for  $\xi_{\text{th}}(T)$ . We then examine what is known about  $l_{\text{in}}(T)$  and compare the two lengths, thus testing for self-consistency.

In the spirit of our model, we write

$$\sigma(T) = 0.1e^2 / \hbar \xi_{\text{th}}(T). \quad (8)$$

For sample 3, the fit of Fig. 2, with  $\Delta = 0$  in Eq. (6), gives  $\sigma(T) = BT$ , with  $B = 0.3 (\Omega \text{ cm})^{-1} / \text{K}$ . Setting  $BT = 0.1e^2 / \hbar \xi_{\text{th}}(T)$  gives

$$\xi_{\text{th}}(T) = \frac{8000 \text{ K}}{T} \text{ \AA} = \begin{cases} 2000 \text{ \AA}, & T = 4 \text{ K} \\ 27 \text{ \AA}, & T = 300 \text{ K} \end{cases}$$

We note that the numerical factor in Eq. (8), set at 0.1, is uncertain by a factor of two or more.

Estimating a value for  $l_{\text{in}}$  in this system is difficult. We know of no reliable theoretical or experimental determinations of  $l_{\text{in}}$  in systems similar to ours, at or very near the  $M-I$  transition. However, some rough estimates can be made. Since we are in the regime where  $\sigma < \sigma_{\min}$ , we expect a strong scattering picture to be valid. In a straightforward random-walk model, we will have

$$l_{\text{in}} = (\tau_{\text{in}} / \tau_{\text{el}})^{1/2} a = (\tau_{\text{in}} v_F a)^{1/2}, \quad (9)$$

where  $a$  is the elastic scattering length,  $\tau_{in}$  is the inelastic scattering time, and  $\tau_{el}$  is the elastic scattering time. Since we are in the strong scattering regime, we have taken  $a$  to be one lattice constant and  $\tau_{el}$  to have the value  $a/v_F$ , where  $v_F$  is the Fermi velocity.

We use Eq. (9) to make an estimate for  $l_{in}(T)$  by assuming that the basic inelastic scattering rate (e.g., by phonons) in  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  will be similar to that in the uncompensated material,  $\text{Na}_x\text{WO}_3$ . At room temperature, a simple Drude model and a value of  $10^5 (\Omega \text{ cm})^{-1}$  for the conductivity of  $\text{NaWO}_3$  (Ref. 16) give a value for  $\tau_{in}$  of  $2 \times 10^{-14}$  sec. We derive a value for  $v_F$  from the band-structure calculations<sup>17</sup> of Kopp, Harmon, and Liu for  $\text{NaWO}_3$ . (For sample 3, the band is occupied by 0.18 electrons per unit cell and we calculate  $E_F$  to have the value 0.68 eV.) For the Na bronzes,  $a = 3.8 \text{ \AA}$ . With these numbers,  $l_{in} = 20 \text{ \AA}$ . Thus, at room temperature,  $l_{in} \approx \xi_{th}$ .

At low temperature, elastic scattering by the disordered lattice dominates conduction in the bronzes, and a good, direct estimate of  $\tau_{in}$  is difficult. A comparison of the value of  $\tau_{in}$  at room temperature to that for copper gives a ratio 0.75. For copper,  $\tau_{in}$  is about  $2 \times 10^{-9}$  sec at 4 K.<sup>18</sup> In the absence of a more direct measurement, we will assume the temperature dependence of  $\tau_{in}$  for the bronzes to be the same as that for copper. With this assumption,  $\tau_{in}$  is about  $1.5 \times 10^{-9}$  sec at 4 K, and Eq. (9) yields a value of 5300  $\text{\AA}$  for  $l_{in}$ . Thus, at 4 K, we meet the condition  $l_{in} > \xi_{th}$ , but not by a large factor.

Our estimates of  $l_{in}$  at 300 and 4 K are, at best, rough. But they suggest that the ratio  $l_{in}/\xi_{th}$  changes quite slowly between 4 and 300 K, and that the assumptions of our model may remain valid over the full temperature range from 1.6 K to room temperature.

In our disordered material, with electrons subject to very strong scattering, a possible contribution in inelastic scattering not present in a clean metal like copper is the disorder-modified electron-electron scattering investigated by, e.g., Schmid,<sup>19</sup> Altschuler and Aronov,<sup>20</sup> and Abrahams *et al.*<sup>21</sup> It is not clear that this theory can be applied to the bronze system in the diffusion regime where  $\sigma < \sigma_{min}$ . Nevertheless, it seems worthwhile to lay some of its results against our data.

One can make guesses about the temperature dependence of  $l_{in}$  if it is determined by the disorder-modified electron-electron scattering. There seems general agreement<sup>19-21</sup> that  $\tau_{in} \propto (kT/E_F)^{-3/2}$ . For the random walk model, with  $l_{in} \propto (\tau_{in})^{1/2}$ , one would have  $l_{in} \propto T^{-3/4}$ . Thus, if  $\sigma(T)$  were dominated by the temperature dependence of  $l_{in}$ , Eq. (7) would predict  $\sigma(T) \propto T^{0.75}$ . For the sample 3 data in Fig. 3 at 4.2 K and below, the fit to  $\nu = 0.99 \pm 0.01$  appears to rule out this temperature dependence.

Use of Eq. (9) and a guess that, for the electron-electron scattering mechanism, we would have  $\tau_{in}/\tau_{el} = (kT/E_F)^{-3/2}$  give a value of 1200  $\text{\AA}$  for  $l_{in}$  at 4.2 K. With our value of 2000  $\text{\AA}$  for  $\xi_{th}$  at 4.2 K, this rough estimate again gives  $l_{in} \approx \xi_{th}$ .

In the absence of a firm determination of  $l_{in}(T)$  and with only limited support from our rough calculations, the conclusion that  $l_{in} \gg \xi_{th}$  must be regarded as speculative. We look upon the agreement between theory and ex-

periment exhibited for samples 3 and 4 as more substantial evidence for the validity of our model.

As one looks at published data for  $\sigma(T)$  in systems whose characteristics might plausibly resemble  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$ , evidence for wide applicability of the model is scant. Data for polycrystalline  $\text{Ge}_{1-x}\text{Au}_x$  given by Dodson, Mochel, McMillan, and Dynes<sup>22</sup> are very similar to ours and seem likely to be well-described by our model. On the other hand,  $\sigma(T)$  measured by the same workers for amorphous samples for the same material shows a different temperature dependence.

There remains the question of why a one-electron model, which ignores electron-electron interactions, appears to successfully predict  $\sigma(T)$  for this system. Carrier compensation may be the answer. Thomas *et al.*<sup>23</sup> have suggested that localization effects may dominate interaction effects in heavily compensated systems. Such systems have many polarizable scatterers and relatively few carriers. Given the evidence that the conduction-electron concentration in metallic  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  is given by  $x - y$ , this bronze can be regarded as a heavily compensated system, and it may not be surprising that localization effects are dominant.

## V. COMPARISON WITH THE TRANSITION IN $\text{Na}_x\text{WO}_3$

We now compare the conductivity transition in  $\text{Na}_x\text{Ta}_y\text{W}_{1-y}\text{O}_3$  with that in cubic  $\text{Na}_x\text{WO}_3$ . Conductivity data<sup>3</sup> for cubic  $\text{Na}_x\text{WO}_3$  extend down only to  $x = 0.22$ . Thus, we do not see the full evolution of the transition in the uncompensated bronze. However, a sample in the tetragonal II crystal structure at  $x = 0.15$  was reported to exhibit semiconducting behavior.<sup>24</sup> And an early analysis by Lightsey,<sup>25</sup> while resting on a somewhat speculative basis, suggested that the transition point for the cubic  $\text{Na}_x\text{WO}_3$  is  $x_c = 0.16 \pm 0.03$ . Taken all together, there is considerable evidence that the values of  $(x - y)_c$  for the two systems, uncompensated and compensated, fall extremely close to one another. We seem to see again a feature that has been noted for a classic semiconductor system,  $\text{Ge:Sb}$ .<sup>23</sup> Compensation, with its accompanying strong potential fluctuations and strong carrier scattering, does not shift the value of  $(x - y)_c$ .

## VI. CONCLUSIONS

Though our data are in good agreement with measurements of Doumerc *et al.*,<sup>2,5</sup> our analysis and conclusions are at some variance with the picture presented by Dordor *et al.*<sup>26</sup> They appear to consider all samples with  $x - y < 0.3$  as lying on the insulator side of the transition, and ascribe the temperature dependence of  $\sigma$  to various hopping mechanisms. We place the transition at  $x - y = 0.18$ , and believe that the temperature dependence of  $\sigma$  for samples near the critical composition represents thermal activation of electrons which are localized at  $T = 0 \text{ K}$ . Although our model is undoubtedly oversimplified, it seems to give a natural explanation of the  $T$  dependence  $\sigma$  for samples near the transition.

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\*Present address: Department of Physics, Ohio State University, Columbus, OH 43210.

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